Journal of Saudi Chemical Society (2013) 17, 199–202

King Saud University

Journal of Saudi Chemical Society

www.ksu.edu.sa
www.sciencedirect.com

ORIGINAL ARTICLE

COD reduction of waste water streams of active pharmaceutical ingredient – Atenolol manufacturing unit by advanced oxidation-Fenton process

Sayyed Hussain [a,*], Shahid Shaikh [a], Mazahar Farooqui [b]

[a] *PG Department of Chemistry, Sir Sayyed College, Aurangabad, India*
[b] *Post Graduate and Research Centre, Maulana Azad College, Aurangabad, India*

Received 13 February 2011; accepted 10 March 2011
Available online 9 April 2011

KEYWORDS

COD reduction;
Active oxidation;
Fenton reagent;
H_2O_2/Fe^{+2};
Atenolol

Abstract Active pharmaceutical intermediates (API) in waste waters have adverse effects on aquatic life and environment. The API have high COD value and low BOD_3 and hence difficult to treat biologically. In this study, advanced oxidation processes (AOPs) utilizing the H_2O_2/Fe^{+2}, Fenton reactions were investigated in lab-scale experiments for the degradation of Atenolol containing waste water streams. The experimental results showed that the Fenton process using H_2O_2/Fe^{+2} was the most effective treatment process. With Fenton processes, COD reduction of wastewater can be achieved successfully. It is suggested that Fenton processes are viable techniques for the degradation of Atenolol from the waste water stream with relatively low toxic by-products in the effluent which can be easily biodegraded in the activated sludge process. Hence, the Fenton process with H_2O_2/Fe^{+2} is considered a suitable pretreatment method to degrade the active pharmaceutical molecules and to improve the biodegradability of waste water.

1. Introduction

Due to high consumption of API by human beings, lot of API pass from the manufacturing units to the environment, through waste water discharged from the factories. This is due to the low biodegradability of the API molecules. In the past two decades, advanced oxidation processes (AOPs) have been proven to be powerful and efficient treatment methods for degrading recalcitrant materials or mineralizing stable, inhibitory, or toxic contaminants. Advanced oxidation processes are those groups of technologies that lead to hydroxyl radical (•OH) generation as the primary oxidant (second highest powerful oxidant after the fluorine). Hydroxyl radicals are non-selective in nature and they can react without any other

* Corresponding author. Mobile: +91 9923320201.
E-mail address: drhussainsyyd@yahoo.com (S. Hussain).

Peer review under responsibility of King Saud University.
doi:10.1016/j.jscs.2011.03.006

Production and hosting by Elsevier

Table 1 Characterization of waste water streams from the Atenolol manufacturing unit.

Waste stream	pH	COD (mg/l)	TDS (mg/l)	Chlorides (mg/l)
Epoxide main ML	Alkaline	30,000–42,000	20,000–35,000	10,000–14,000
Washing ML	Alkaline	7500–20,000	12,000–18,000	4000–7000

additives with a wide range of contaminants. These hydroxyl radicals attack organic molecules by either abstracting a hydrogen atom or adding a hydrogen atom to the double bonds. It makes new oxidized intermediates with lower molecular weight or carbon dioxide and water in case of complete mineralization. There are few reports regarding use of AOP for the treatment of pharmaceutical waste (Tekin et al., 2006; Emolla et al., 2010) dyes and pigments (Mass and Chaudhari, 2005; Muruganandham and Swaminathan, 2004; Arslan et al., 1999; Kuo, 1992), printing ink waste (Ma and Xia, 2009), and sulfate ion (Wang et al., 2008). This paper aims at studying the effect of the operating conditions (pH, H_2O_2/Fe^{+2} ratio, reaction time) of the advanced oxidation processes using H_2O_2/Fe^{+2} for the different waste water streams containing Atenolol and Atenolol spiked water. The H_2O_2/Fe^{+2} is used as the oxidant. The optimum conditions of the Fenton process were tried for different Atenolol containing waste water streams.

2. Materials and methods

Waste water streams of Atenolol manufacturing unit from Waluj area of Aurangabad were collected and they were analyzed for pH, TDS, COD and chlorides (Table 1). The chemicals used such as hydrogen peroxide solution (33%, w/w) heptahydrated ferrous sulfate ($FeSO_4{\cdot}7H_2O$) were all of commercial grade from SD fine Chem. Ltd. All reagents employed were not subjected to any further treatment. Water used throughout was double distilled.

3. Experimental set-up

All experiments were performed in a Round bottomed flask in a laboratory. Compressed air was used for purging to keep the reaction mass mixing. The addition of the H_2O_2 and ferrous sulfate was done manually at room temperature. The reaction was carried in batch mode for different waste water stream separately and in combination with the proportion ratio equal to the actual generation. After the completion of the reaction time, the samples were removed from the round bottomed flask and the samples were made alkaline (pH 10–12) using sodium hydroxide. These removed samples were digested for 1 h on a hot water bath and kept overnight and then filtered to remove the insoluble ferric hydroxide. The filtrate collected was used for the estimation of COD as per APHA (APHA, 1995). The sample was refluxed with a known excess of potassium dichromate for two hours. After digestion, the excess dichromate was titrated against standard ferrous ammonium sulfate.

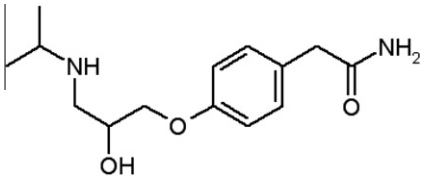

Figure 1 Structure of Atenolol.

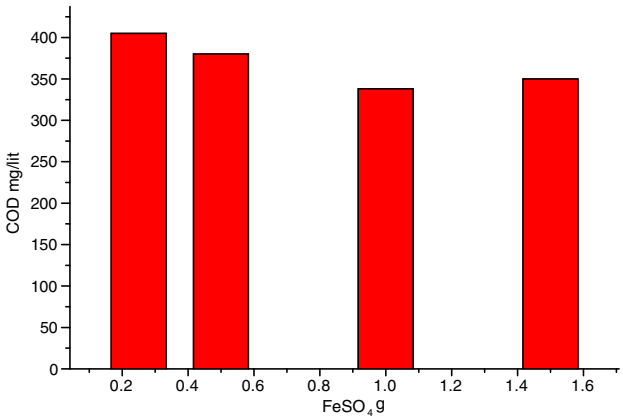

Figure 2 COD variation with $FeSO_4$.

4. Results and discussion

The molecular formula of Atenolol is $C_{14}H_{22}N_2O_3$ (Fig. 1). The IUPAC name is RS-4-(2-hydroxy-3-isopropylaminopropoxy) phenylacetamide. The results of Fenton process to water spiked with Atenolol are given in Table 2. (Fig. 2).

It was observed that the percentage reduction of COD approaches 66% with increasing volume of H_2O_2 and $FeSO_4$. In Fenton process organic compounds oxidized by hydroxyl radicals produced which is strong oxidant. The various steps involved in the production of OH^- is given

Table 2 Reduction of COD after 4 h by AOP.

Effluent qty-spiked with Atenolol (ml)	pH	Initial COD	H_2O_2 (ml)	$FeSO_4$ (g)	COD after 4 h (mg/l)	Percentage reduction of COD
500	2.0	694	10	1.0	370	46.6
500	2.0	694	15	1.5	347	50.0
500	2.0	694	20	2.0	280	59.6
500	2.0	694	25	2.5	234	66.0

Table 3 Reduction in COD with variation of $FeSO_4$.

S. no.	Qty of H_2O_2 (ml)	Qty of $FeSO_4$ (g)	COD initial (mg/l)	COD after 4 h (mg/l)
1	10	0.25	694	405
2	10	0.5		380
3	10	1		338
4	10	1.5		350

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH^{\cdot}.$$
$$Fe^{2+} + OH^{\cdot} \rightarrow Fe^{3+} + OH^-$$
$$Fe^{3+} + H_2O_2 \rightarrow Fe\text{–}OOH^{2+} + H^+$$
$$Fe\text{–}OOH^{2+} \rightarrow Fe^{2+} + OOH^{\cdot}$$
$$Fe^{2+} + OOH^{\cdot} \rightarrow Fe^{3+} + OOH^-$$
$$Fe^{3+} + OOH^{\cdot} \rightarrow Fe^{2+} + O_2 + H^+$$
$$H_2O_2 + OH^{\cdot} \rightarrow H_2O + OOH^{\cdot}$$

In which there are large cyclic reactions which utilize the Fe^{+2} or Fe^{+3} ions as a catalyst to decompose H_2O_2. The hydroxyl radical produced in the above reaction has very high oxidation potential ($E^0 = +2.80$ V) second only to fluorine

It is observed that the Atenolol spiked water is degraded with AOP. The maximum COD reduction was found to be 66% with the peak condition of H_2O_2 at 25 ml and ferrous sulfate at 2.5 g in 4 h duration. The initial COD was found to be 694 mg/l with varying amounts of $FeSO_4$ and H_2O_2, but keeping the ratio same, it was observed that (Table 2) COD reduction increases with increase in the amount of $FeSO_4$. In the second set of experiment, we varied only the amount of $FeSO_4$ and rest conditions kept constant. This also shows (Table 3) the same trend, i.e. decrease in COD with the increase in the amount of $FeSO_4$ (Fig. 3).

The effect time also studied maintains pH 2 and $FeSO_4$, H_2O_2 constant. It was observed that the percentage reduction increases up to 66% in 4 h (Table 4). The effect of time on COD is shown in Fig. 3. The COD removal was carried out at three different pH values in the acidic range which shows that maximum reduction is at pH 2 (Table 5).

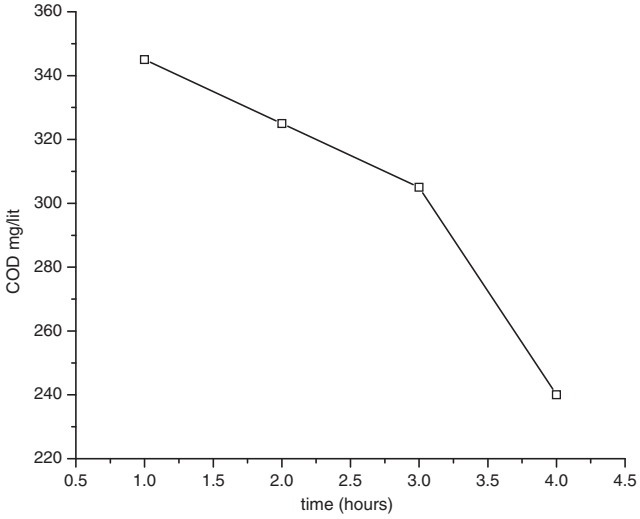

Figure 3 Effect of time on COD.

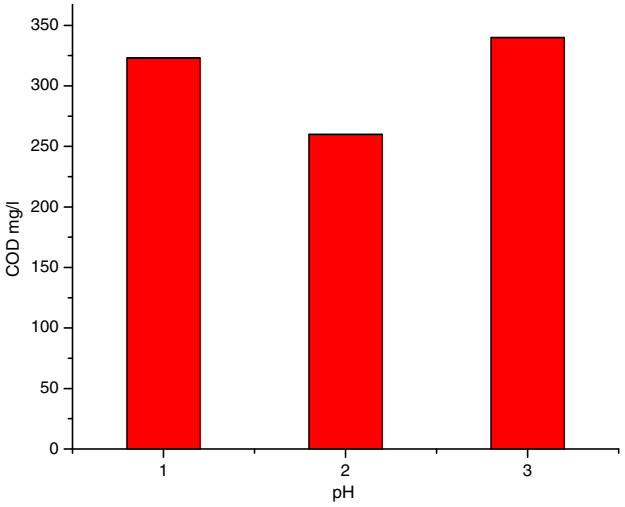

Figure 4 Effect of pH.

Table 4 Effect of time on reduction of COD from waste water.

S. no.	Qty of H_2O_2 (ml)	Qty of $FeSO_4$ (g)	Volume of spiked sample	Spiked impurity (mg/l)	COD initial (mg/l)	Time (h)	COD after (mg/l)	% Reduction
1	25	2.5	500	Atenolol		1	345	50
2	25	2.5	500	Atenolol	694	2	325	53
3	25	2.5	500	Atenolol		3	305	56
4	25	2.5	500	Atenolol		4	240	65

Table 5 Effect of pH on COD removal.

Initial COD (mg/l)	H_2O_2 (ml)	pH	$FeSO_4$ (g)	COD after 4 h (mg/l)	Percentage reduction of COD
571	25	1.0	2.5	323	43
571	25	2.0	2.5	260	54
571	25	3.0	2.5	340	40

From the above table it is evident that the rate of the degradation of the Atenolol molecule is maximum at pH 2.0. Maximum COD reduction is upto 54% at this pH.

With the trial on the spiked water with Atenolol and AOP on it show about 66% COD reduction, the said method is very effective and economical. This process can be used as a pretreatment to the activated sludge process, thereby making the biodegradability easy in aeration tank of the activated sludge process. The Fenton treatment for Atenolol after streams can help in reducing the ETP construction cost as the COD load to ETP will be reduced with the application of Fenton process (Fig. 4).

References

APHA, 1995. Standard method for the examination of water and waste water, 19th ed. American public health association, Washington, DC.

Arslan, I., Balcioglu, A., Tuhkanen, T., 1999. Oxidative treatment of simulated dye house effluent UV and near UV light assisted Fenton's reagents. Chemosphere 39, 2767–2783.

Emolla Emad, S., Chaudhari Malay, Mohammad, Eltoukhy, Meselhy, 2010. The use of artificial neural network (ANN) for modeling of COD removal from antibiotic aqueous solution by the Fenton's process. J. Hazard. Mater. 179, 127–134.

Kuo, D.G., 1992. Decolorizing dye waste water with Fenton's reagent. Water Res. 26, 881.

Ma Xiang, Jung, Xia, Hui-long, 2009. Treatment of water based printing ink waste water by Fenton process combined with coagulation. J. Hazard. Mater. 162, 386–390.

Mass, R., Chaudhari, S., 2005. Adsorption and biological discoloration of azo dye reactive red-2 in semicontinuous anaerobic reactor. Process Biochem. 40, 699–705.

Muruganandham, M., Swaminathan, M., 2004. Decolonization of reactive orange-4 by Fenton's and photo Fenton oxidation technology. Dyes Pigments 63, 315–321.

Tekin, Husein, Bilkay, Okan, Ataberk Selali, S., Balta Togla, H., Ceribasi Haluk, I., Sanin Dielk, F., Dilek Filiz, B., 2006. Use of Fenton oxidation to improve the biodegradability of pharmaceutical waste water. J. Hazard. Mater. 136 (2), 258–265.

Wang, Xiao-Jun, Song, Yang, Mai, Jun-Shong, 2008. Combined Fenton oxidation and aerobic biological process for the treatment a surfactant waste water containing abundant sulfate. J. Hazard. Mater. 160, 344–348.